CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA.

No. XIII.

A Study of some of the Derivatives of Mono- and Dichlor-Salicylic Acids.

By Dr. John Marshall.

(*Read before the American Philosophical Society, April 5th,* 1878.)

This work was undertaken at the suggestion of Dr. Edgar F. Smith, to whom, for his many kindnesses shown during the progress of the investigation, I would express my best thanks.

Of late years the monohydroxyl substitution products of benzoic acid—salicylic acid and its isomers—have been completely investigated, and many interesting facts regarding the nature of these acids revealed. Of the uninvestigated derivatives of salicylic, metaoxybenzoic and paraoxybenzoic acids remain yet the mono and dichlorinated compounds. In the following pages will be described my results obtained from the study of simply the mono and dichlor acids derived from salicylic acid.

These new compounds that I have obtained show in several instances the stability imparted to compounds into which one or more chlorine atoms have been introduced.

Monochlorsalicylic Acid.

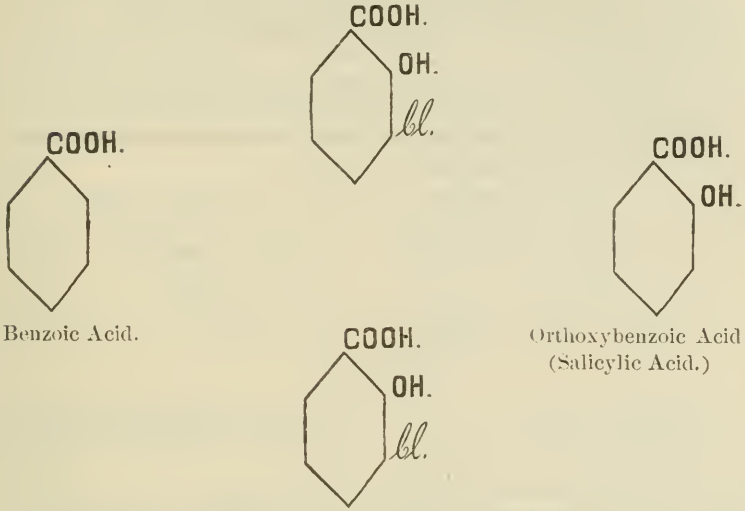
$$C_6 H_3 Cl O H C O O H.$$

Fusing point 172°.

This acid was first obtained by Hübner and Brenken (Berichte der deutschen Chem. Gesellschaft, 1873, p. 174). Their manner of producing it consisted in mixing ordinary salicylic acid with an excess of carbon bisulphide and conducting chlorine into the mixture, which was continually shaken. When the calculated amount of chlorine had been introduced, the contents of the flask were emptied into a large basin and evaporated to dryness on a water bath. The dry residue was taken up in water and crystallized from this in needles which fused at 172° C. The lead, silver, opper and barium salts were simply described, further investigation being neglected.

Hübner and Weiss produced metachlorbenzoic acid, and by nitration, amiding and forming the Diazo-compound, and subsequently treating the latter with water they obtained metachlororthoxybenzoic acid, fusing at

171° C. and perfectly identical with the monochlorsalicylic acid. The graphic formula of the latter would be represented by the following:



Benzoic Acid.

Orthoxybenzoic Acid (Salicylic Acid.)

Metachlororthoxybenzoic Acid.

Cahours in 1845 described a similar acid, "*Acide monochlorosalicylique*" (Ann. Chim. Phys. 13, 106), but never obtained it in a pure condition.

The method I pursued to secure the acid for my investigations was the following: A weighed amount of the purest salicylic acid that could be obtained (melting at 155° C.) was brought into a capacious flask, and a rather large quantity of concentrated acetic acid added. Into this mixture a calculated amount of dry chlorine gas was conducted. The heat generated by the reaction soon caused the solution of the salicylic acid. The liquid gradually acquired a yellowish-brown color. When the calculated amount of chlorine had been introduced, water was added in large excess and the solution allowed to stand several hours before filtering off the acid that had separated out in large white flocculent masses. After thoroughly washing the acid with cold water, it was boiled with a large quantity of barium carbonate and water. The liquid was filtered from the excess of the latter salt, evaporated and allowed to stand over night. Upon examination crystals of barium dichlorsalicylate were usually discovered. The mother liquid poured off from these and further concentrated yielded the barium salt of the monochlor acid. This salt I invariably recrystallized several times, and then added dilute hydrochloric acid to its aqueous solution which precipitated the acid in perfectly white flocculent masses.

The acid was recrystallized several times from water separating out from this menstruum in long colorless needles which fused at 172° C. In warm water the acid is readily soluble.

Inasmuch as this acid differs from salicylic in having one atom of chlorine, its antiseptic properties might be enhanced, and owing to its ready solubility would therefore render it preferable to salicylic acid.

An aqueous solution of the acid mixed with ferric chloride gives a beautiful violet coloration.

An analysis of the material thus prepared gave the final proof that the compound formed was the desired monochlorsalicylic acid.

.1417 grms. dried acid burned with coarse and fine lead chromate gave 48.13 % carbon, and 3.00 % hydrogen.

Calculated per cent.			Found per cent.
C_7	= 84	= 48.69 %	48.13 %
H_4	= 4	= 2.89 %	3.00 %
Cl	= 35.5	= 20.58 %	——
O_3	= 48.	= 27.84 %	——
	171.5	100.00	

SALTS.

For a more complete recognition of the acid the following salts were made and aualyzed :

Barium Monochlorsalicylate.

$$(C_6 H_3 Cl OH COO)_2 Ba + 3 H_2 O.$$

Obtained by boiling the aqueous solution of the acid with an excess of barium carbonate and filtering. The filtrate upon concentration and standing for some time, yielded white, bright, shining crystals of this salt. In cold water it is soluble, and when the liquid is warmed the compound dissolves very readily.

Water Estimation.

0.2000 Grms. air-dried salt lost upon heating for four hours at 170° C., .0200 Grms. H_2O = 10.00 % H_2O.

The calculated per centage of water for 3 molecules H_2O = 10.11 %.

Calculated.			Found.
$(C_6 H_3 Cl OH COO)_2 Ba$	= 480	= 89.89 %	——
$+ 3 H_2O$	= 54	= 10.11 %	10.00 %
	534	100.00	

Barium Estimation.

0.121 Grm. anhydrous salt was placed in a platinum crucible, a few drops of sulphuric acid was then added and this evaporated to dryness. .0594 Grm. barium sulphate were obtained, corresponding to .0349 Grm. barium = 28.83 % Ba.

Calculated per cent.			Found per cent.
$(C_6 H_3 Cl OH COO)_2$	= 343	= 71.45 %	——
Ba	= 137	= 28.55 %	28.83 %
	480	100.00	

POTASSIUM MONOCHLORSALICYLATE.

$$C_6 H_3 Cl OH C O O K.$$

Formed by boiling a solution of the Barium salt with a calculated amount of potassium sulphate and evaporating the filtrate; or by boiling the free acid with a slight excess of potassium carbonate.

The salt crystallizes from its aqueous solution in long colorless needles, very soluble in cold and hot water. Analysis showed it to be anhydrous.

Potassium Estimation.

.1168 Grm. dried salt evaporated in a platinum crucible with sulphuric acid, gave .0491 Grm. potassium sulphate, which corresponds to .0220 Grm. potassium = 18.83% K.

Calculated per cent.			Found per cent.
$C_6 H_3 Cl OH COO$ =	171.5 =	81.48%	——
+ K =	39.1 =	18.52%	18.83%
	210.6	100.00	

SODIUM MONOCHLORSALICYLATE.

$$C_6 H_3 Cl OH COO Na.$$

I prepared this salt in a manner similar to the preceding potassium compound. From concentrated aqueous solution it crystallizes in short, straw-colored needles, easily soluble in cold or warm water. It is anhydrous.

Sodium Estimation.

0.2986 Grm. dried salt treated just as in the preceding analysis, gave .1081 Grm. sodium sulphate, which corresponds to .0350 Grm. sodium = 11.72% Na.

Calculated per cent.			Found per cent.
$C_6 H_3 Cl OH COO$ =	171.5 =	88.18%	——
+ Na =	23. =	11.82%	11.72%
	194.5	100.00	

LITHIUM MONOCHLORSALICYLATE.

$$C_6 H_3 Cl OH COO Li + 2 H_2O.$$

I made this salt by boiling the free acid with a slight excess of Lithium carbonate. The filtered solution was then strongly evaporated and placed over sulphuric acid to crystallize. After long standing the salt appeared in large, broad, colorless plates—very hard—which were united to aggregated masses. After several recrystallizations the salt was analyzed.

Water Estimation.

.1876 Grm. air-dried salt heated for three hours at 130° C. lost .0030 Grm. H_2O = 1.59% H_2O.

2 molecules H_2O require 1.67%.

Lithium Estimation.

.1846 Grm. of the perfectly dried salt were treated with a few drops of concentrated sulphuric acid and evaporated to dryness in a platinum crucible. .0566 Grm. lithium sulphate were obtained = .0072 Li = 3.90% Li.

Calculated per cent.			Found per cent.
$C_6 H_3 Cl OH COO$ =	171.5 =	96.08%	——
+ Li =	7. =	3.92%	3.90%
	178.5	100.00	

ETHERS.

The introduction of various hydro-carbon residues yielded me in most instances well crystallized and stable derivatives. The method pursued in all cases for the production of these compounds was to treat the silver salt of the acid with a monohalogen derivative of the hydro-carbon to be introduced: e. g.

$$C_6 H_3 Cl OH COO Ag + C_x H_y I = Ag I + C_6 H_3 Cl OH COO C_x H_y.$$

Methyl Iodide.—$C H_3 I$. This I prepared as follows: 50 Grms. iodine were mixed in a flask with 20 Grms. methyl alcohol and 5 Grms. amorphous phosphorus gradually added. As heat is generated in this reaction, the flask was kept in a basin of cold water. The mixture was first subjected to distillation after having stood twelve hours. The first distillate was in all cases treated with sodium hydrate and calcium chloride, and then redistilled.

Ethyl Iodide.—$C_2 H_5 I$. Made this compound according to the directions given for its production: 1 part amorphous phosphorus, 5 parts ethyl alcohol, and 10 parts iodine were treated as above. Boils at 72°C.

Isobutyl Iodide.—$CH_2 I CH (CH_3)_2$. 50 Grms. iodine, 50 Grms. isobutyl alcohol, and 8 Grms. amorphous phosphorus were distilled together. A heavy, oily liquid boiling at 119°C.

Acetyl Chloride.—$CH_3 CO CL$. Prepared this by distilling equal parts of anhydrous acetic acid and phosphorus pentachloride.

Description of Ethers.

METHYL MONOCHLORSALICYLATE.

$$C_6 H_3 Cl OH COO CH_3.$$

Fusing point, 48°C.

Silver monochlorsalicylate was heated together with an excess of methyl iodide in a sealed tube at 140°C for twelve hours, and upon opening the tube and expelling the excess of methyl iodide, a residual oil was left. Even when kept in a cold place solidification was not effected. As I

thought that this very probably was nothing more than a decomposition product—the result of too intense heating—I treated a second portion of the silver salt in a similar manner, taking care, however, not to let the temperature become too great. The thermometer indicated 103°C for three hours. The color of the liquid in the tube was dark red. The tube was opened and the liquid filtered off from the silver iodide which was washed with alcohol, and the solution then evaporated almost to dryness. Upon allowing the solution to stand over night, I observed the next morning that the liquid had solidified perfectly. The mass was removed from the beaker glass, reduced to a fine powder, and after being exposed to the air for several days, it was dissolved in alcohol.

Upon warming the solution the mass dissolved readily, and upon cooling the compound separated out in long, colorless needles. These fused at 48°C, upon recrystallization I discovered that the fusing point remained constant, and the substance was then subjected to an analysis.

Carbon and Hydrogen Estimation.

.2235 Grm. well dried substance burned with lead chromate, gave .4228 Grm. CO_2 = .1150 Grm. carbon, corresponding to 51.45% carbon. And further, .0851 Grm. H_2O = .0095 Grm. hydrogen, equaling 4.25% hydrogen.

Calculated per cent.			Found per cent.
C_8 = 96	=	51.47%	51.45%
H_7 = 7	=	3.75%	4.25%
O_3 = 48	=	25.74%	——
Cl = 35.5	=	19.04%	——
186.5		100.00	

Cahours (Ann. Chim. Phys. 10. 343) mentions a methyl ether of chlorsalicylic acid produced by the action of chlorine upon methyl salicylic acid. It was difficult to obtain it pure. I believe this to be entirely different from my compound above described.

Ethyl Monochlorsalicylate.

$$C_6 H_3 Cl OH C O O C_2 H_5.$$

I have succeeded in forming this compound, but as I have never had it in pure enough condition to make an analysis, I give merely my experience in its formation. Time and again I heated the pure silver salt with perfectly pure ethyl iodide, but when I searched for the resulting ether, I obtained nothing more than a dark heavy liquid that remained in this condition under all circumstances. That this was nothing else than a decomposition product I learned afterwards. High heat is not required for the formation of this compound, it is produced just as soon as the silver salt and ethyl iodide are shaken well with each other, the reaction is indicated by the increase of temperature that may be noticed by placing the hand on the vessel containing the mixture. A portion of the silver salt with ethyl

iodide was heated in a sealed tube in a water bath for three hours, the tube was then opened, contents thrown upon a filter and the silver iodide washed with alcohol, and the filtrate evaporated on a water bath almost to dryness. The compound crystallized in stellated masses fusing at 110° C.

Isobutyl Monochlorsalicylate.

My attempts to obtain this ether were futile. With the greatest care I never succeeded in obtaining the compound, that I may have destroyed it by too intense heating, if it was formed, I do not consider possible, as I not only heated a mixture above 100° C., but also in luke-warm water, the latter temperature is necessary to effect the formation of silver iodide. I think that very likely simple exposure to the air in process of drying caused the decomposition of the ether into the acid.

Acetyl Monochlorsalicylate.

$$C_6 H_3 Cl O H COO, O C C H_3.$$

Fusing point 149° C.

I obtained this compound by heating the silver salt a number of hours with acetyl chloride at a temperature not over 130° C. The contents of the tube were placed on a filter, the silver chloride washed with alcohol and the filtrate evaporated upon a water bath and then allowed to crystallize, the ether separated in dark acicular masses, these were pressed well between paper and fused at 147° C. The compound was recrystallized four times from alcohol, in which it is readily soluble. The pure ether fuses at 149° C. A combustion gave the above composition. Water decomposes the ether.

Carbon and Hydrogen Estimation.

.0763 Grm. dried substance gave 50.00% carbon and 3.93% hydrogen.

Calculated per cent.		Found per cent.
$C_9 = 108$	$= 50.34\%$	50.00%
$H_7 = 7$	$= 3.26\%$	3.93%
$O_4 = 64$	$= 29.85\%$	
$Cl = 35.5$	$= 16.15\%$	

Action of Alcoholic Ammonia upon Methylmonochlorsalicylate.

By treating this ether with ammonia the object was to displace the *OH* group in the carboxyl with the group NH_2, according to the following equation:

$$C_6 H_3 Cl OH CO O CH_3 + N H H H = C_6 H_3 Cl OH C O N H_2 + C H_3 O H.$$

This change I effected and obtained.

MONOCHLORSALICYLAMIDE

$C_6 H_3 Cl OH CO N H_2$.

Fusing point 222°–223° C.

Produced by heating Methylmonochlorsalicylate with an excess of alcoholic ammonia in a sealed tube. The tube was kept in the oven for twelve hours, it was then removed, and the alcoholic solution strongly concentrated upon a water bath. When the liquid cooled a mass of needle-like crystals separated out.

When pure the compound fuses at 222°–223° C. Very soluble in warm alcohol.

When the alcoholic ammonia was poured upon the ether the liquid assumed a beautiful pale blue fluorescence. Upon heating this entirely disappeared.

Carbon and Hydrogen Estimation.

I. .0510 Grm. substance dried at 100° C. for one hour, gave .0930 Grm. CO_2 = .0253 carbon = 49.5% carbon. Water estimation a failure.

II. 0.1713 Grm. substance dried at 125° C. gave .3041 Grm. CO_2 = .08293 carbon. = 48.41% carbon. And .0554 H_2O = .0061 hydrogen = 3.56% hydrogen.

Calculated per cent.		Found per cent. I.	Found per cent. II.
C_7 = 84	= 48.97%	49 5 —	48.41%
H_6 = 6	= 3.49%		3.56%
O_2 = 32	= 18.66%		——
Cl = 35.5	= 20.74%		——
N = 14	= 8.14%		——
171.5	100.00		

MONOCHLORNITROSALICYLAMIDE.

$C_6 H_2 NO_2 Cl O H CO N H_2$.

Fusing point 192° C.

This compound shows to what extent the presence of the NH_2 group influences the introduction of new radicals. The ordinary monochlorsalicylic acid when treated with fuming nitric acid does not yield nitrochlorsalicylic acid as would be expected, but the carboxyl group breaks up and chlordinitrophenols result. To obtain monochlornitrosalicylic acid the chlorsalicylic acid must be treated with nitric acid very strongly diluted with acetic acid. When chlorsalicylamide, however, is dissolved in fuming nitric acid but one product is obtained—the above mentioned—Monochlornitrosalicylamide. The stability imparted to the compound by the amide group allows the reaction to occur without any decomposition.

After the amide has been dissolved in nitric acid, water is added to the solution, which causes the precipitation of the nitro compound in yellow flocculent masses. These I brought upon a filter, washed well with cold distilled water and then boiled up with potassium carbonate. By strongly evaporating the solution the potassium salt crystallized out. After purification the acid was set free with dilute hydrochloric acid. The acid recrystallized from water showed the constant fusing point 192° C. In cold water it is only slightly soluble and dissolves readily in large quantities of warm water. It crystallizes from aqueous solutions in long, slightly yellow-colored crystals—needles.

The following salts were made and analyzed:

SALTS.

Potassium Monochlornitrosalicylamide.

$$C_6 H_2 NO_2 Cl O K CO N H_2.$$

I obtained this by boiling the free acid with a slight excess of potassium carbonate. From the concentrated filtrate the salt deposits in long yellowish-red needles. Easily soluble in water.

Potassium Estimation.

.0460 Grm. air-dried salt were evaporated in a platinum crucible with sulphuric acid. There resulted .0146 Grms. $K_2 SO_4$ = 14.93% potassium.

Calculated per cent.			Found per cent.
$C_6 H_2 Cl NO_2 O C O N H_2$	= 215.5	= 84.70%	——
+ K	= 39.	= 15.30%	14.93%
	354.5	100.00	

Barium Monochlornitrosalicylamide.

$$(C_6 H_2 Cl NO_2 O C O N H_2)_2 Ba.$$

I obtained this salt by boiling the free acid with barium carbonate and evaporating the filtrate. The salt crystallizes in short, thick needles, of a deep blood-red color. It is only soluble in a rather large quantity of boiling water.

Barium Estimation.

.2006 Grm. well dried salt were dissolved in water and the barium precipitated as sulphate. Obtained .0805 Grms. $Ba SO_4$ = 23.66% Ba.

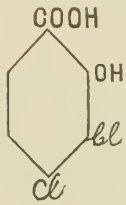
Calculated per cent.			Found per cent.
$C_6 H_2 NO_2 Cl O C O N H_2$ / $C_6 H_3 NO_2 Cl O C O N H_2$	= 431	= 75.89%	——
+ Ba	= 137	= 24.11%	23.66%
	568	100.00	

DICHLORSALICYLIC ACID.

$$C_6 H_2 Cl_2 OH COOH.$$

Fusing point 214.

This acid I made according to the method described by Smith, E. F. (American Philosophical Society, Proceedings June 15, 1877.) It formed in rather large quantities along with the monochlor derivative of salicylic acid. The acid was obtained from its barium salt. In cold water it is insoluble, an excess of the boiling liquid being necessary to effect its solution. It fuses at 214° C., and crystallizes from water in arborescent masses. Very soluble in alcohol. The acid is *Parachlormetachlororthoxybenzoic acid* and is graphically represented thus :



That this compound is different from that of Cahours (Annalen der Chemie und Pharmacie—52, 340, 341 pp.), is not only proven by the salts as Smith has done, but also from the fact that the ethers derived from it are not analogous to those published by Cahours.

The ethers I have made were produced in a similar manner to those of monochlorsalicylic acid.

METHYL DICHLORSALICYLATE.

$$C_6 H_2 Cl_2 OH C O O C H_3.$$

Fusing point 142° C.

I obtained this compound by heating a quantity of silver dichlorsalicylate with an excess of methyl iodide in a sealed tube, the temperature being about 135° C. Upon adding methyl iodide to the salt some action was observed, attended by a decided increase of temperature, the heating in a closed tube, therefore, continued but a few hours. The tube was then allowed to cool, opened and the contents washed with alcohol upon a small filter. In the filtrate needles separated out and were dissolved by adding more alcohol and applying heat. The solution was then evaporated to a small volume and allowed to crystallize, this it did almost immediately.

The crude material fused at 135° C., after pressing the substance well between filter paper, it was again dissolved in an excess of alcohol, from which it afterwards separated in large colorless needles that reflect light strongly.

The fusing point after repeated recrystallizations was discovered to be constant at 142° C.

In alcohol the ether is difficultly soluble. Water decomposes it.

Carbon and Hydrogen Estimation.

0.1974 Grm. dried substance burned with coarse and fine lead chromate, gave 0.3196 Grm. CO_2 = .0830 Grm. carbon = 43.56% carbon; and further, .0551 Grm. H_2O = .0060 Grm. hydrogen = 2.71% hydrogen.

Calculated per cent.		Found per cent.
C_8 = 96 =	43.47%	43.56%
H_6 = 6 =	2.71%	2.71%
Cl_2 = 71 =	32.12%	——
O_3 = 48 =	21.70%	——
221	100.00	

In the Ann. Chem. Phys. 10, 343, Cahours mentions a methyl dichlor-ether he obtained by allowing chlorine to act upon methyl salicylic acid.

From boiling alcohol needles of the ether were secured which fused at about 100° C., very considerably lower than the above described compound.

Ethyl Dichlorsalicylate.

$$C_6\,H_2\,Cl_2\,OH\,C\,O\,O\,C_2\,H_5.$$

Fusing point 47° C.

Obtained in the usual manner. From the first alcoholic solution it separated as a dark colored oil, which, after being pressed between filter paper, dissolved in warm alcohol, and upon cooling, the compound separated in beautiful colorless needles. The fusing point was found to be 47° C.

Carbon and Hydrogen Estimation.

0.2072 Grm. well dried substance burned with lead chromate, gave .3418 Grm. CO_2 = 45.51% carbon; and .0808 Grm. H_2O = 4.30% hydrogen.

Calculated per cent.		Found per cent.
C_9 = 108 =	45.96%	45.51%
H_8 = 8 =	3.41%	4.30%
Cl_2 = 71 =	30.21%	——
O_3 = 48 =	20.42%	——
235	100.00	

Smith first described this compound (Proceedings Am. Phil. Society, June 15, 1877).

Cahours obtained a similar derivative by the action of chlorine upon ethyl salicylate. Broad colorless needles. Fusing point not given.

ISOBUTYL DICHLORSALICYLATE.

$$C_6 H_2 Cl_2 OH C O O C H_2\text{–}C H (C H_3)_2.$$

Fusing point 188°–190° C.

In the case of the monochlor acid the production of this derivative was not attended with success. With the dichlor acid the formation of the isobutyl compound followed without any difficulty, the usual method being employed, viz.: heating the silver salt and isobutyl iodide in a sealed tube at 150° C. The contents of the tube were treated with alcohol, thus dissolving the new compound. The alcoholic filtrate was evaporated almost to dryness and put away in a cool place. In the lapse of a couple of hours the liquid in the beaker had solidified. The mass was removed from the vessel, thoroughly dried between filter paper, removing in this manner the greater portion of adherent isobutyl iodide, then dissolved in alcohol and allowed to crystallize. Warty-like masses appeared of fine, minute, almost colorless needles. In alcohol the compound is exceedingly soluble. In pure water, even when boiling, it was discovered to be almost insoluble, decomposing after a time.

To extract the compound, cold water was added to a concentrated alcoholic solution. This was done several times and the compound then crystallized from a mixture of alcohol and water. It crystallizes in needles, fusing at 188°–190° C.

An analysis yielded the following results:

Carbon and Hydrogen Estimation.

0.1190 Grm. dried substance burned with lead chromate, gave 0.2200 Grm. CO_2 = 0.06 Grm. carbon = .5042% carbon. Further .0525 Grm. H_2O = .0058 Grm. hydrogen = 4.87% hydrogen.

Calculated per cent.			Found per cent.
C_{11} =	132 =	50 19%	50.42%
H_{12} =	12 =	4.56%	4.87%
Cl_2 =	71 =	27.00%	——
O_3 =	48 =	18.25%	——
	263	100.00	

ACETYL DICHLORSALICYLATE.

$$C_6 H_2 Cl_2 OH C O O CO C H_3.$$

With the monochlorsalicylic acid I had no special trouble to obtain this derivative, but with this acid the most careful work apparently failed to yield it. The material employed to effect its formation was perfectly pure.

I invariably obtained a product, but this when purified and analyzed, gave results that indicated the compound was nothing more or less than the original dichlorsalicylic acid.

Unless the alcohol which I employed as a solvent for the compound caused the decomposition of the latter, I am at a loss to know to what my failure to obtain it should be ascribed.

Both the mono and dichlor acids were acted upon by benzoyl chloride, but as I have not yet ascertained anything positive in regard to the resulting compounds, statements of their properties, &c., are withheld for the present.

DICHLORSALICYLAMIDE.

$$C_6 H_2 Cl_2 OH C O N H_2.$$

Fusing point 209° C.

The same course was pursued here for the obtainment of this compound, as has already been described under the heading of *Action of Ammonia upon methylmonochlorsalicylate.* The heating in a sealed tube was continued through twelve hours. The temperature never extending above 100° C. The contents of the tube removed and evaporated, deposited small nodular crystals. These upon recrystallization became perfectly white in color, but retained the form of the nodules, which appeared to be composed of densely united needles. The compound dissolves readily in alcohol. The pure compound fused at 209° C. It was not subjected to a combustion.

The fluorescence that was exhibited when alcoholic ammonia was poured upon the methylmonochlorsalicylate, was not near as beautiful as that observed in this case. Heat caused its disappearance.

By comparing the results of this investigation with similar derivatives of ordinary salicylic acid, the evident stability shown by most of the ethers of mono and dichlor salicylic acids, will not fail to be observed, and the cause for this seems to be due to the presence of negative chlorine, since this apparent stability shows itself from the moment of its introduction. Of the four ethers obtained from the monochlor acid, two, the ethyl and isobutyl derivatives appear to lack the decided crystalline character exhibited by the rest. With the dichlorine compounds the acetyl is the only one that has indicated any signs of non-stability. A comparison, too, of the salts of the different acids, shows the influence exerted by the presence of chlorine. All are fine crystalline compounds.

TABULAR VIEW OF MONO- AND DICHLOR-SALICYLIC ACIDS AND THEIR DERIVATIVES.

Monochlorsalicylic Acid. $C_6H_3ClOHCOOH$. (Hübner & Brenken.)	172°	Long colorless needles, readily soluble in water.	$(C_6H_3ClOHCOO)_2Ba + 3H_2O$. Colorless shining plates. Easily soluble in water. (Marshall.)	$C_6H_3ClOHCOOK$. Long colorless needles. Very soluble in hot and cold water. (Marshall.)	$C_6H_3ClOHCOONa$. Short straw-colored needles, easily soluble in water. (Marshall.)
					$C_6H_3ClOHCOOLi + 2H_2O$. Large colorless, broad plates. Rather soluble in water. (Marshall.)
		$C_6H_3ClOHCOOCH_3$. Fuses 48° C. Long colorless needles rather soluble in alcohol. (Marshall.)		$C_6H_3ClOHCONH_2$. Fuses 222°-223° C. Needles soluble in warm alcohol. (Marshall.)	
		$C_6H_3ClOHCOOC_2H_5$. Fuses 110° C. Stellated masses. (Marshall.)		$C_6H_2NO_2ClOHCONH_2$. Fuses at 192° C. Slightly yellow colored needles. Soluble in water. (Marshall.)	
		$C_6H_3ClOHCOOC_4H_9$? (Marshall.)		$C_6H_2NO_2ClOKCONH_2$. Yellowish-red needles. Readily soluble in water. (Marshall.)	
		$C_6H_3ClOHCOOCOCH_3$. Fuses 189° C. Acicular masses soluble in alcohol. (Marshall.)		$(C_6H_2NO_2ClOCONH_2)_2Ba$. Short thick needles. Red in color. Soluble in a large quantity of boiling water. (Marshall.)	
Dichlorsalicylic Acid. $C_6H_2Cl_2OHCOOH$. (Smith.)	211°	$C_6H_2Cl_2OHCOOCH_3$. Fuses 142° C. Long, colorless needles. Difficultly soluble in alcohol. (Marshall.)	$C_6H_2Cl_2OHCOOC_2H_5$. Fuses 17° C. Colorless needles. (Smith.)	$C_6H_2Cl_2OHCOOCH_2—CH(CH_3)_2$. Needles fusing at 188°-190° C. (Marshall.)	
				$C_6H_2Cl_2OHCOOCOCH_3$? (Marshall.)	
			Colorless needles, fusing at 17° C. (Marshall.)	$C_6H_2Cl_2OHCONH_2$. Fuses 209° C. White nodular crystals soluble in alcohol. (Marshall.)	